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Transistor Effects and in situ STM of Redox Molecules at Room Temperature

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Abstract – Inorganic transition metal complexes were identified as potential candidates for transistor-like behaviour in an electrochemical STM configuration at room temperature. The theoretical background has been established based on condensed matter charge transfer theory. It predicts a distinct increase of the tunnelling current close to the equilibrium potential, i. e. if molecular bridge states are tuned into resonance with the Fermi levels of the enclosing electrodes. The complexes display robust electrochemistry on Au(111) electrode surfaces. STM images at molecular resolution give detailed insight into the surface structure. STS experiments are on the way to probe putative transistor-like behaviour.

Index Terms – Charge transfer, conductivity, molecular electronics, resonant tunneling transistors, transition metal compounds.

I. INTRODUCTION

Objectives of emerging nanoscale chemistry at semiconductor and metal surfaces are to map and control the two- or even three-dimensional structure of molecular entities ranging from small organic molecules to transition metal complexes and larger architectures such as proteins, DNA, and dendrimers.

With a view on molecular electronics, there is a particular interest in understanding and controlling the electronic coupling between the molecular bridge states and the Fermi levels of the enclosing electrodes in order to achieve pronounced switching effects between "on" and "off" states. Within the last few years, these concepts have been described both theoretically and experimentally in increasing detail. As a result, functional devices such as switches, rectifiers, diodes and transistors seem to be within reach.

Most studies so far, however, have concentrated on organic molecules under ex situ conditions, i. e. either in air or in vacuum, and at low temperatures [1]. On the other hand, operation at room temperature is clearly needed. We propose a different approach to investigate

switching effects in small molecular entities. It relies on similarities between a transistor and an electrochemical in situ scanning tunnelling microscope (STM) configuration, i. e. in an electrochemical environment at room temperature. In such a setup, the analogue of source, drain and gate contacts are working electrode, STM tip and reference electrode, respectively. At constant bias, molecular bridge states can be tuned into resonance with the Fermi levels of tip and working electrode by changing the reference potential while the tunnelling current is monitored (scanning tunnelling spectroscopy, STS). According to charge transfer theory adapted to such a configuration by Ulstrup and Kuznetsov [2], the tunnelling current will increase once resonance is reached, resulting in the desired transistor effect. This resonance is, moreover, expected to be close to the redox potential of a particular state.

We have identified inorganic transition metal complexes with Os, Co, and Ru as central ions to be promising candidates for testing these theoretical expectations. These complexes are stable in at least two redox states with sufficiently low-lying electronic states, their ligand chemistry is well understood, and they can relatively easily be modified, e. g. with respect to the linker group at the metal/molecule interface. With the theoretical frame set and detailed electronic structure calculations on the way, we are now heading at the experimental verification of this effect by combining a variety of electrochemical techniques on atomically planar single-crystal gold and platinum surfaces with in situ STM and STS.

II. EXPERIMENTAL

All chemicals were of highest available grade, H₂O was supplied by a Millipore system (Milli-Q Housing). The complexes [Os(bpy)₂(p0p)₂](PF₆)₂ (**1**) and [Os(pby)₂(p2p)₂](PF₆)₂ (**2**) were prepared by refluxing

[Os(bpy)₂Cl₂]₂·2H₂O and AgNO₃ in a 1:1 ethylene glycol/H₂O solution until a grey precipitate was formed. After removing the precipitate, either p0p or p2p were added and refluxing continued for 96 hours. After removing unreacted ligand and addition of a concentrated aqueous solution of ammonium hexaphosphate, the product was washed with H₂O, dried with diethylether and purified by column chromatography. The identity of the compounds was checked by NMR spectroscopy. (bpy = 2,2'-bipyridyl; p0p = 4,4'-bipyridyl; p2p = 1,2-bis(-4-pyridyl)ethane)

Au(111) electrodes were prepared as published before [3]. For STM a Au(111) disc electrode (10 mm · 1 mm) was purchased from Surface Preparation Laboratory. Electrodes were annealed in a H₂-flame, cooled in H₂O-saturated air and transferred to the stock solution of a particular complex immediately.

The stock solutions were prepared in a concentration range of 10 to 100 μM in a mixture of H₂O/DMF 2:1 (m/m). Electrodes were soaked overnight, then rinsed with Millipore H₂O and electrolyte (0.1 M HClO₄).

An electrochemical Autolab system controlled by a GPES software package (Ecochemie, Netherlands) was used including custom-made electrochemical (glass) cells. A freshly prepared reversible hydrogen electrode (RHE) and a Pt wire served as reference and counter electrode, respectively. The reference potential was checked with a saturated calomel electrode (SCE) after each experiment. The Au(111) electrodes were employed in a hanging-meniscus configuration. Prior to each experiment, the electrochemical cell was deoxygenated by purified Ar (Chrompack O₂ filter) and a steady flow of Ar was maintained at all times during operation.

A PicoSPM instrument (Molecular Imaging Co., USA) with a bipotentiostat for independent control of substrate and tip potential was used in constant-current mode. The custom-made three-electrode Teflon cell was equipped with two Pt wires serving as reference and counter electrodes. The reference potential was checked with a SCE reference electrode after each experiment. The concentration of either (1) or (2) in the electrolyte was in the range of 1 to 10 μM.

III. THEORY

The theoretical background of transistor functionality is described in the literature [2]. In the fully adiabatic case where both electron transfer steps, working electrode/bridge and bridge/tip, accord with the adiabatic limit, the tunnelling current can be described by equation (1) assuming two symmetric metal contacts:

$$i_{tunn}^{ad} = \frac{1}{2} \cdot \exp(eV_{bias}) \cdot \frac{\omega_{eff}}{2\pi} \cdot \exp\left(-\frac{E_R + eV_{bias}}{4k_B T}\right) \times \cosh^{-1}\left[\frac{\left(\frac{1}{2} - \gamma\right)eV_{bias} - e\xi\eta}{2k_B T}\right] \quad (1)$$

κ is the transmission coefficient, ρ the level density in the two metals, ω_{eff} a characteristic (nuclear) frequency, E_R the molecular reorganization energy, γ and ξ the fractional potential drops of bias and sample potential at the redox center, and η the overpotential, i. e. the difference between equilibrium potential and sample potential. All other parameters have their usual meaning.

If bias potential drop γ at the redox center equals one half, the maximum of the tunnelling current is found at $\eta = 0$, i. e. at the equilibrium potential. By modulating the reference potential, molecular redox levels can thus be tuned in and off resonance resulting in an "on" and "off" state analogous to a transistor-like device. For a detailed description of the electronic properties of such a device, theoretical frames need to be substantiated by experimental data, specifically regarding the metal/bridge interface and the central metal ion.

IV. EXPERIMENTAL RESULTS

Prior to any in situ STM experiment, the stability of the electrochemical response from the complexes (1) and (2) and a corresponding potential window was characterized by cyclic voltammetry on single-crystal Au(111) electrodes as shown in Fig. 1.

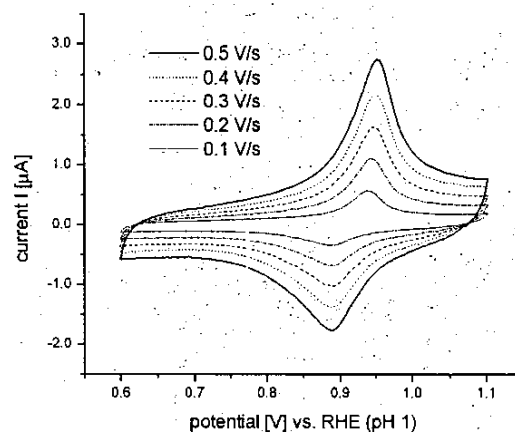


Fig. 1. Cyclic voltammograms of compound (1) at different scan rates v from 0.1 V/s to 0.5 V/s; electrolyte: 0.1 M HClO₄

A plot of the peak current I_p vs. the scan rate v yielded a linear correlation, indicating that the observed electron transfer process indeed originates from a surface-confined species (not shown). The electrochemical response was stable for at least several hundred potential scans.

In situ STM investigations under the same conditions have revealed that the monolayers of both compounds (1) and (2) consist of two different domain types. The major part of the electrode surface seems to be disordered, but some areas display highly ordered structures where images of molecular resolution were obtained. Fig. 2 shows a high-resolution in situ STM image of compound (2).

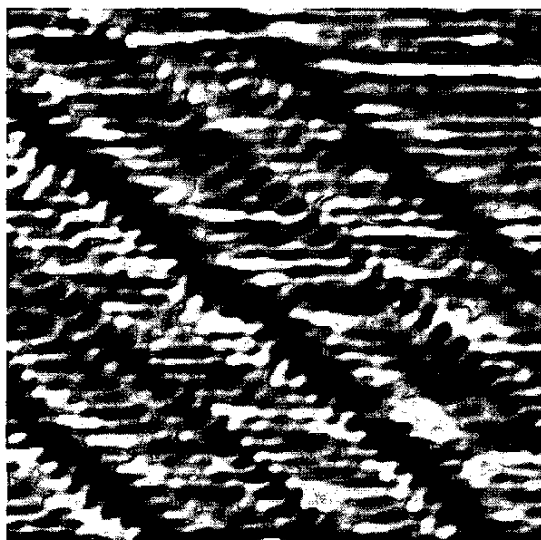


Fig. 2. In situ STM image of compound (2) in 0.1 M HClO_4 ; area: $(12.5 \text{ nm})^2$; $E_s = +0.25 \text{ V}$, $V_{\text{bias}} = -0.2 \text{ V}$, $I_{\text{set}} = 50 \text{ pA}$ (all potentials vs. SCE)

A double-striped feature is clearly visible that is composed of two individual lines each displaying molecular substructure. The diameter of such an individual line is approximately 19 \AA . This is very similar to the diameter of (2) along one of the linker ligands p3p (ca. 17 \AA). We therefore conclude that, at least in the highly ordered domains, only one ligand is bound to the surface while the other one is pointing into the solution, presumably being protonated. This finding is in line with previous work by Forster et al. who came to the same conclusion for a comparable complex, $[\text{Os}(\text{bpy})_2(\text{p3p})_2](\text{PF}_6)_2$, based on electrochemical data [4].

At present, STS experiments are in progress to probe the effect of the sample potential on the conductivity of individual molecules, i. e. on their contrast in a STM

experiment. Two approaches that both promise to reveal transistor effects are currently being tested, namely constant-height and constant-current mode. The former is quite demanding experimentally because it requires extremely stable conditions. On the other hand, it yields directly the I_t vs. E_s correlation. In constant-current mode, the information obtained from STM imaging is rather a height change from the piezo element coupled to the feedback loop of the scanner. The response therefore also depends on the settings of the feedback loop. This approach, however, provides spatially resolved data for individual molecules. Thus, a combination of both techniques thus seems to be most desirable.

V. CONCLUSIONS

We have synthesized two compounds of a larger class of transition metal complexes identified as promising candidates for displaying transistor-like features in their molecular room temperature conductivity and in an electrochemical environment. The theoretical framework has been established. The electrochemical characterization of both compounds has shown that they form highly stable self-assembled monolayers on Au(111). STM images down to molecular resolution have been obtained that allow for insight into details of their surface organization. Their electrochemical properties support our design strategy and, presently, detailed STS investigations are on the way to probe the electronic properties of the molecules on the single-molecule level.

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